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Effect of Seasonal Variation in Southern Pine Terpenes on Dryer Emissions

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## EFFECT OF SEASONAL VARIATION IN SOUTHERN PINE TERPENES ON DRYER EMISSIONS

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### ABSTRACT

Terpene concentrations measured at some mills have large swings of a seemingly seasonal nature. The question to be resolved is whether these variations are attributable to wood handling and mill operations or to biological factors associated with tree growth. Information in the available literature deals with monoterpene production and release associated with foliage, not wood. This paper describes the experiments and results of a study designed to compare the amount of monoterpenes from loblolly pine (*Pinus taeda*) increment cores to volatile organic compound (VOC) emissions from total hydrocarbon analyses. Some seasonal trends were noted but cannot yet be attributed to specific climatological influences.

### INTRODUCTION

This study was begun in 1996 because a southern pine oriented strand board (OSB) mill reported wide variability in Method 25A VOC emissions measured in the field. Two measurements could not be reproduced even when taken on the same day; it was unknown whether this result was due to random variability in the raw material itself, systematic seasonal variations, or to handling. An additional issue was that the sporadic measurements typically made in the field may include unrecognized seasonal effects, atypical of average annual emissions. The mill was interested in alternative means of making measurements and sent samples of fresh flakes to the Institute of Paper Science and Technology for analysis. These samples were wrapped, stored cold, and dried in a 130° C tube furnace equipped to monitor total hydrocarbon emissions (Banerjee *et al.*, 1998). The results of laboratory analyses from the first two year's samples demonstrated that the VOC concentrations varied by as much as 500% (from ~ 300 :g/g to 1500 :g/g on a wet basis).

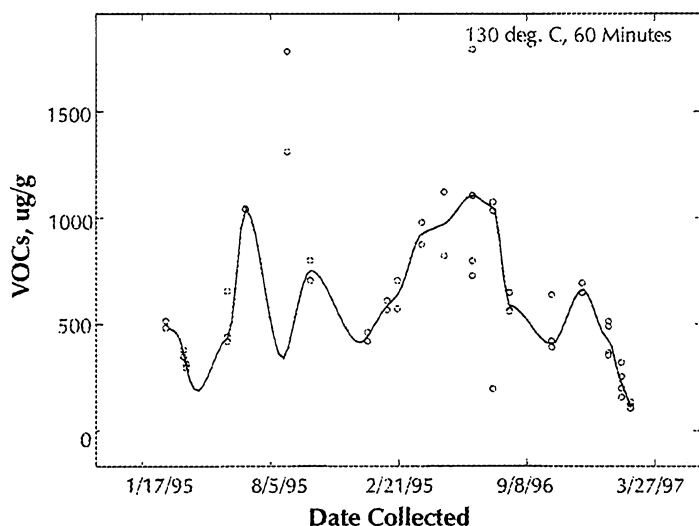
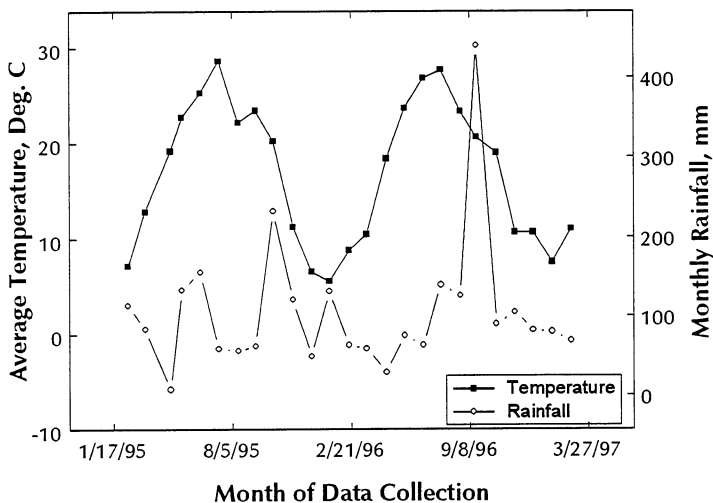


Figure 1: Results of laboratory analyses of southern pine flakes from a North Carolina OSB mill.

Consistent with the mill's previous Method 25A measurements, significant variation was apparent even within single sampling dates. There appeared to be some degree of interactive relation with the ambient temperature and rainfall data (Figure 2), but (at least in part because of the data variability) it was not clear that there was a significant cause-and-effect relationship. It seemed likely that other factors such as handling, storage conditions or sampling at the mill might be affecting the laboratory measurements. The company requested further work, including measurements of VOCs from standing trees, to verify the scatter in the flake VOC measurements and to determine, if possible, the reasons for the large variation in the measured VOC concentrations. This work is still in progress, but this report provides the information available at this time.



**Figure 2: Rainfall and temperature data corresponding to North Carolina OSB mill location.**

As part of this investigation the available literature was reviewed to determine if variability in total VOC (monoterpene) content had been studied before. There are numerous articles describing the variation of VOCs from resinous conifers, but most of the available information has been collected from studies of needles, seedlings and twigs. No information was found that described the variation of VOCs in the trunks of standing trees. A number of studies were found that describe the changes in monoterpene composition on a seasonal basis for various species, but most of these were conducted over periods of one year or less. For example, Zafra and Garcia-Peregrin (1976) surveyed the composition of essential oil distilled from *Pinus halepensis* twigs for part of one year (from October through June) and found that the principal components were sabinene and  $\alpha$ -pinene. In this study, there was approximately twice as much sabinene as  $\alpha$ -pinene; the  $\alpha$ -pinene proportion seemed to decrease slightly during the cooler months (by about 10%), while the sabinene proportion increased commensurately. The small month-to-month differences noted for the concentrations of terpenes in the twigs were seen in needles as well. An investigation of *Pinus elliottii* by Bin *et al.* (1992) found that the amount of "turpentine" steam-distilled from resin from tapped trees increased from July to November, and that the major constituents were  $\alpha$ -pinene and  $\beta$ -pinene.  $\alpha$ -Pinene constituted about two-thirds of this mixture, although the proportion of  $\beta$ -pinene was somewhat greater during the cooler months. Lerdau and Stilts (1992) found "seasonal declines" in monoterpene concentration but constant emissions from foliage; Lerdau *et al.* (1995) later reported a strong effect of temperature and seasonality on emissions. He-Ping (1995) reported that the relative contents of some volatile terpene compounds collected from the foliage of *Pinus tabulaeformis* varied between the summer and the winter months; for example, the  $\alpha$ -pinene and  $\beta$ -pinene concentrations both increased by about 25% during the summer months compared to the January samples. There are evidently important genetic and physiological aspects of terpene biosynthesis that affect tree-to-tree variations. Raffa (1991) has also reported that the monoterpene concentration in grand fir (*Abies grandis*) increased nearly four-fold after insect attack. All of this information did little to answer our immediate question.

## EXPERIMENTAL

An experiment was planned in early 1997 to compare VOC emissions from fresh southern pine flakes with samples obtained from standing trees. In a continuation of the initial study, samples of southern pine flakes were requested on a periodic basis from the North Carolina OSB mill for laboratory VOC analysis, and plans were made to monitor the monoterpene concentrations in a longitudinal study using twelve straight, well-formed loblolly pine trees (*Pinus taeda*) (each approximately 39 cm (15 inches) in diameter and forty years old) in the Mississippi State University's John W. Starr Memorial Forest. These trees were naturally reseeded, not from a plantation, and all of the trees should have a somewhat similar genetic provenance because they were located in the same area. From March, 1997, until September of that year one 0.5 cm (0.2 inch) diameter increment core was taken from each tree per month for analysis of the monoterpene and resin acid content according to the analytical procedure described at the end of this paper. The first core from each tree was taken at breast height, and successive cores were offset by several inches both horizontally and vertically/upwards (Figure 3). To prevent infection, each hole was plugged with a maple dowel immediately after the core was taken. Each core was then divided into three portions prior to analysis (inner third, center third and outer third) to enable us to study the intra-tree monoterpene distributions should this prove useful at a later date.

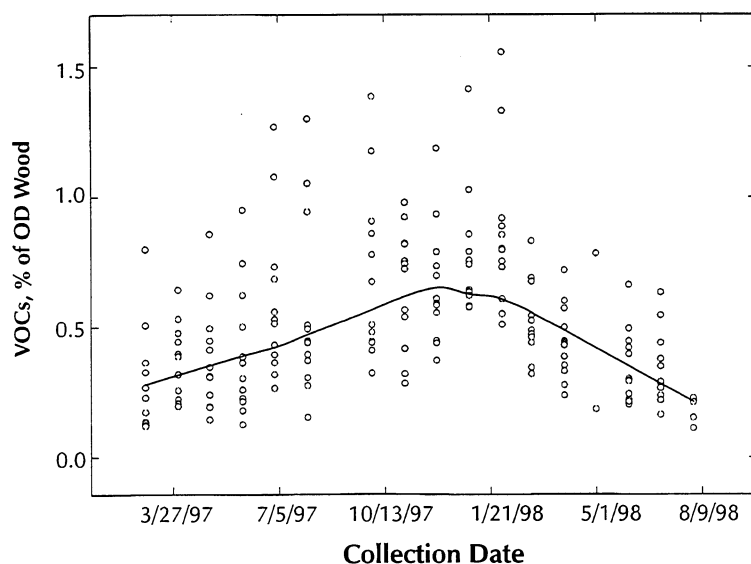


**Figure 3: One of the sampled trees with two increment-cored locations marked.**

In September of 1997 the sample trees (although clearly marked) were cut by an overzealous logging equipment demonstrator, and after a one-month hiatus the experiment was continued with another twelve trees in a nearby location. These trees are of similar age and size to the original sample trees. Like the original sample, the second group was naturally reseeded and was not part of a plantation planting. One of the twelve trees was cut and dissected during the month of December, 1998, to determine whether the repeated sampling and plugging caused injury-induced resin to bleed internally and bias the data, but no evidence was seen to indicate that this was a problem.

The potential for handling and storage conditions to affect VOC measurements was recently addressed by the Mississippi State University Forest Products Laboratory. In a series of controlled experiments, southern pine chips from freshly-cut 16- to 18-year old trees were taken directly from a paper mill chipper. Samples of these chips were analyzed immediately (using five replications) for both  $\alpha$ -pinene and  $\beta$ -pinene (which together comprise most of the monoterpenes in loblolly pine); additional samples, sterilized using sodium azide and maintained at room temperature, were measured every two or three days for two weeks. Approximately one-third of the  $\alpha$ -pinene was lost during the first week, after which no further losses were noted.  $\beta$ -Pinene concentrations did not appear to be affected. Based on these results it is concluded that the handling and storage history of the flakes sent from the mill might affect the monoterpene concentrations of some samples.

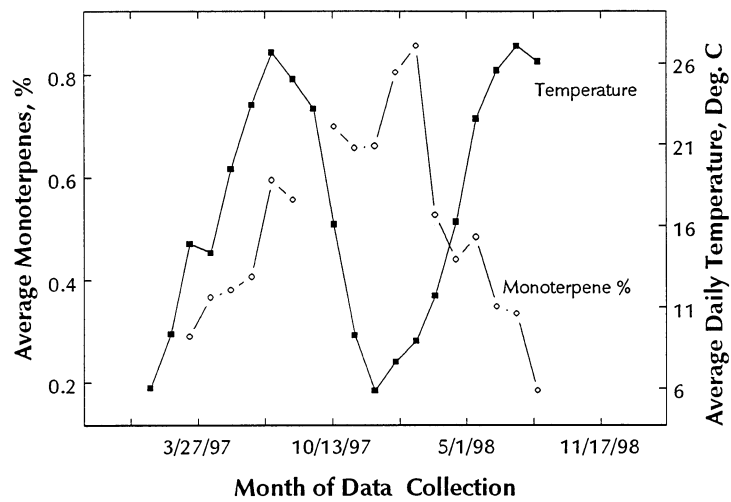
Figure 4 shows the monoterpene concentration data collected and analyzed through August, 1998; a locally-weighted (loess) regression line (span=0.5) has been drawn through the data to help illustrate the overall trend in the face of such evident variability.



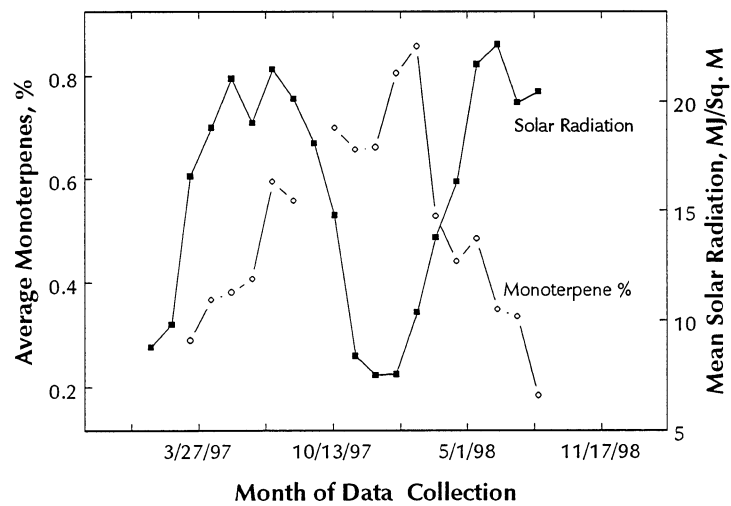
**Figure 4: Total VOCs as a percent of oven-dry (OD) wood from the longitudinal study of 12 loblolly pine trees in Starkville, Mississippi (loess regression line shown overlaid on data, span = 0.5).**

Figure 4 shows that there are slight differences from one year to the next (no doubt partly caused by sampling different trees), but most of the change in concentration appears to be due to season or some associated climatological component. Based on these data it appears that loblolly pine trees have a greater monoterpene content during the cooler months of the year. In Mississippi this also means that loblolly pine trees have a greater monoterpene content during the rainiest months of the year.

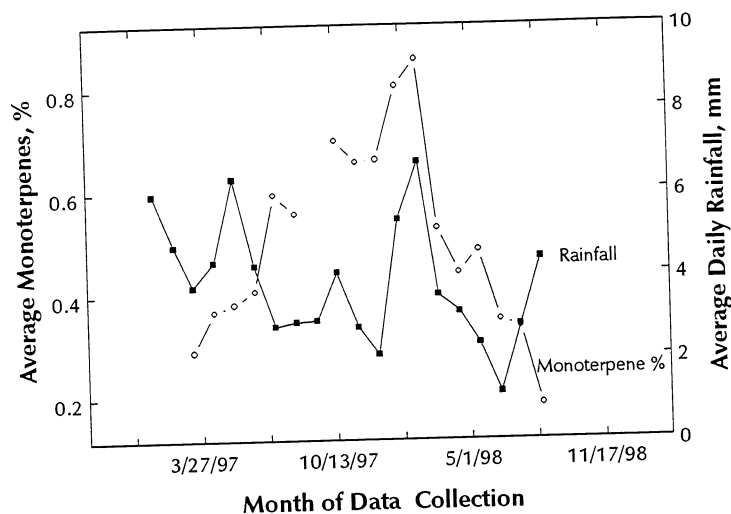
Because of reports which describe the variation of monoterpenes in needles of various conifers as functions of temperature, sunlight or moisture (*e.g.*, Lincoln and Langenheim (1978), Zafra and Garcia-Peregrin (1976)), climatological data were obtained from the USDA Agriculture Research Center at Mississippi State University (<ftp://marlin.csrumsu.ars.ag.gov>) and the average monoterpene concentrations were plotted as functions of these influences (Figures 5, 6, and 7). Obviously the solar radiation and temperature data are highly correlated, so it is not surprising that these plots are similar. During the first year of sampling, the average monoterpene concentration increased as temperature increased then continued to climb to its highest point during the cooler months; this trend did not repeat during the second year of sampling. As can be observed from the graphs, during the second year the monoterpene concentrations actually decreased to the lowest levels observed during this experiment. Possibly this indicates an interactive effect with rainfall, as the summer of 1998 was considerably drier than the summer of 1997. It is also worthwhile to note here that samples containing the highest monoterpene concentration in a given month may have ranked much lower in other months. The climatological data will be statistically examined for correlative influences on the monoterpene concentrations after additional data have been collected.



**Figure 5: Average daily temperatures in Starkville, Mississippi vs monoterpene contents in sampled trees (percent of oven-dry wood).**

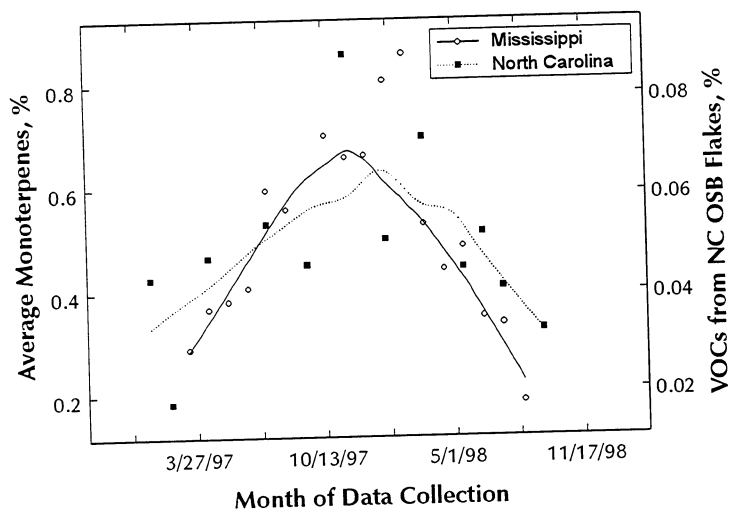


**Figure 6: Average daily solar radiation in Starkville, Mississippi vs monoterpene contents in sampled trees (percent of oven-dry wood).**



**Figure 7: Average daily rainfall in Starkville, Mississippi vs monoterpene contents in sampled trees (percent of oven-dry wood).**

The Mississippi data (analyzed on an oven-dry wood basis) were compared with the Institute of Paper Science and Technology data for the North Carolina OSB flakes (analyzed on a green weight basis). Figure 8 shows two loess regression lines (span = 0.5) based on averaged data for each sampling date; considering the differences in both analytical techniques and in the geographical origins of the specimens, the Figure 8 curves are remarkably similar.



**Figure 8: Comparison of the amounts of monoterpenes from Mississippi tree analyses with VOCs from North Carolina OSB flakes.**

## SIGNIFICANCE OF FINDINGS

There is a great deal of variability from sample to sample during any given analysis period, and consequently our findings may not be typical of the population of loblolly pine trees. In the trees we sampled, however, we found that the typical monoterpene concentrations in standing trees might vary by as much as 200% to 300% during the course of a year (depending on how the "typical" data measure is chosen). Between the lowest and the highest monoterpene concentrations recorded to date in the longitudinal study there is a difference of more than 700% over time. There is no reason to believe that the variability might be less for trees sampled from other locations. The Mississippi and North Carolina data patterns are similar, suggesting that the data presented



here are indicative of real trends and that they are not artifacts of analytical techniques. Seasonal influences appear to affect the monoterpene concentration in the stemwood of these loblolly pines, but even though there are specific short-term correlations with temperature and sunlight intensity it seems likely that there is an interactive effect with rainfall or some other unidentified influence. A more detailed study of possible interrelationships among climatological factors and monoterpene concentrations in trees is underway. It seems likely that a significant part of the variability in OSB flake dryer emissions can be traced to physiological effects, and the rest can be attributed to handling and other factors.

## **ANALYSIS METHODS**

### **Increment Core Study**

One 0.5 cm (0.2 inch) increment core was taken from each of the selected loblolly pine trees per month. The cores were placed in pre-weighed test tubes, stored at 0° C and returned to the laboratory for analysis. Specimens were processed by adding 10 mL of methylene chloride and 1 mL of 1000 :g/ml 1,4-dichlorobenzene, and a known standard concentration was placed in a clean test tube and stored with the samples until the analysis was completed. Samples were sonicated for one hour and concentrated in a hot water bath. One mL of 1000 :g/mL diphenylmethane in methylene chloride was added as an internal standard. One mL was taken from the concentrate and 0.1 mL of diazomethane was added prior to analysis on a Varian 3600 gas chromatograph equipped with a J&W DB-5 30 meter capillary column and flame ionization detector. Target monoterpenes included:  $\alpha$ -pinene,  $\beta$ -pinene, camphene, myrcene, limonene, fenchyl alcohol, borneol, methyl eugenol and 4-allylanisole. Increment cores were dried in an oven overnight at 103° C to obtain the dry weight of the wood.

### **VOCs from OSB Flakes**

The methodology used to measure VOCs from drying flakes is described in Banerjee *et al.* (1998).

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